

HEMATITE FORMATION AND GROWTH IN GALE CRATER SEEN THROUGH MSL CHEMIN X-RAY DIFFRACTION DATA.

M. Szczerba¹, E. B. Rampe², T. S. Peretyazhko³, T. F. Bristow⁴, R. V. Morris², D. F. Blake⁴, D. T. Vaniman⁵, S. J. Chipera⁵, R. T. Downs⁶, R. M. Hazen⁷, D. W. Ming², S. M. Morrison⁷, A. H. Treiman⁸, A. S. Yen⁹, V. M. Tu³, M. T. Thorpe¹⁰, C. N. Achilles¹⁰, D. J. Des Marais⁴, J. P. Grotzinger¹¹, N. Castle⁵, P. C. Craig⁵, E. M. Hausrath¹², S. L. Simpson², B. Tutolo¹³ IGS PAN, ²NASA JSC, ³Jacobs - NASA JSC, ⁴NASA Ames, ⁵PSI, ⁶Univ. Arizona, ⁷Carnegie Institution for Science, ⁸LPI, ⁹JPL, ¹⁰NASA GSFC, ¹¹Caltech, ¹²UNLV, ¹³Univ. Calgary.

Introduction: For more than 10 Earth years, the Mars Science Laboratory (MSL) *Curiosity* rover has been studying modern sediments and ancient sedimentary rocks deposited by lacustrine, fluvial, deltaic, and eolian processes in Gale crater. The mineral and X-ray amorphous abundances in rocks and sediments have been quantified via X-ray diffraction (XRD) data from the CheMin instrument [1,2]. The received data demonstrate significant mineralogical variations within the stratigraphy, including changes in the type and abundances of Fe-oxides/oxyhydroxides silica polymorphs, phyllosilicates, and sulfate minerals [e.g., 2-4].

Characterizing Fe-oxides/oxyhydroxide minerals in Gale crater is especially important for constraining past aqueous environments because their formation depends on a variety of conditions, including pH, Eh, temperature, and salinity. Hematite, magnetite, goethite, and akaganeite have been identified by CheMin in different portions of the stratigraphic section.

Hematite is the most prevalent Fe-bearing oxide mineral and has been detected (>1 wt.%) in 34 of the studied 36 drill targets. Variations in hematite crystallite size were reported in association with Vera Rubin ridge [5], which has a strong hematite signature in orbital reflectance spectroscopy [e.g., 6]. Here, we calculate hematite crystallite sizes and shapes for the entire stratigraphic section to date, to characterize trends and evaluate the processes by which hematite formed and transformed in Gale crater.

CheMin instrument: CheMin XRD data are collected in transmission geometry from a Co source [1]. The angular range is ~4 to 52° θ and the angular resolution is ~0.3° $\Delta\theta$ (although it varies over the angular range). The 2D XRD patterns are converted to 1D patterns using the GSE software [7].

Selected samples: From all of the drilled samples, 20 samples were selected for detailed peak analysis of hematite reflections because these samples contain more than 1.5 wt.% hematite. In the analyzed 2 θ angular range, four hematite peaks are observed: (012), (104), (110) and (113). The most intense ones are: (104) and (110) (Fig. 1a). All phases identified in these samples were included in XRD fitting and peak analysis to account for possible hematite peak overlaps with other mineral phases.

Data processing: We calculated instrumental contributions to peak shapes of the 0.26-0.32 ° θ broad peaks measured by CheMin. For this purpose, a diffractogram of the quartz-beryl 3:97 standard (measured on sol 740) was fitted, taking into account contributions from Co lamp spectrum, receiving slit size, and tube beam spot size for exact primary and secondary goniometer radii. Full width at half maximum (FWHM) dependence on 2 θ angle was then tuned by addition of gaussian and hat convolutions dependent on 2 θ angle. All further analyses were performed for fixed instrumental contribution optimized in this procedure.

Two methods of whole powder pattern modelling (WPPM) were performed: 1) WPPM method with one volume-weighted mean size of crystallites [8]; 2) WPPM with independent fit of mean sizes of crystallites for all major four hematite peaks, using Double-Voight convolutions [9]. Relative intensities were corrected by employing preferred orientation modelled with spherical harmonics.

Mean crystallite sizes: Results of the WPPM method 1) show that among all studied martian hematite samples, there is significant variation of volume weighted crystallite sizes. The smallest crystallites (ca. 3 nm) are stratigraphically at the highest positions, while the largest ones (ca. 40 nm) are in the lower parts of the stratigraphic column, as well as in Vera Rubin ridge [5]. The largest size values cannot however be calculated very precisely because of imprecision of the methodology, as in this case the dominant contribution to peak widths is from instrumental broadening, not from crystallite sizes.

Crystallite sizes in crystallographic directions: Hematite crystallizes in the trigonal R-3c space group, therefore its unit cell has equal a and b dimensions. Its (110) peak corresponds to directions in the a-b plane, whereas (104) and (113) peaks have significant contribution along the c direction.

Calculated volume-weighted crystallite sizes for peaks (110) and (104) show that the smallest martian hematite crystallites are of equant thickness, ca. 2-5 nm in every direction (Fig. 1b). Increase of calculated crystallite thickness is similar in (104) and (110)

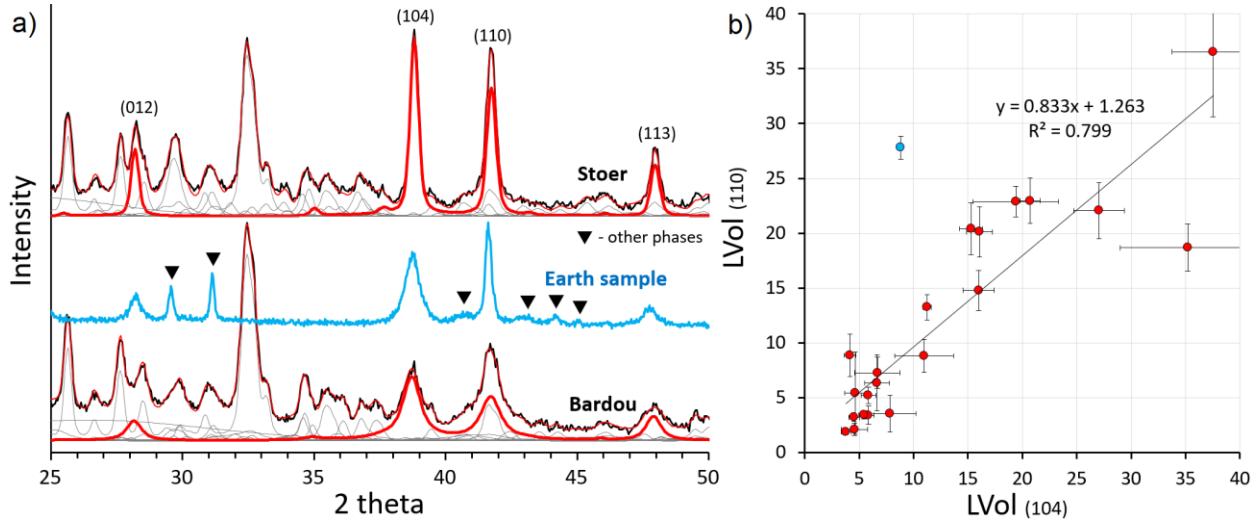


Fig. 1. a) Comparison of two diffractograms of martian samples containing high percentage of hematite (Bardou and Stoer, Gale crater) with diffractogram of terrestrial Ediacaran sample of hematite formed by weathering in East-European craton (significant difference in FWHM of (104) and (110) peaks is visible). Peaks of hematite in martian samples are marked with thick red lines, other phases with thin grey lines. b) Mean volume-weighted crystallite thicknesses of (110) versus (104) reflections for Gale crater samples (red) and terrestrial sample from Fig. 1a (blue).

directions (Fig. 1b). Sharpening of these peaks can be due to an increase of crystallite sizes and, to some extent, due to a decrease of microstrain broadening (which is caused by lattice imperfections, such as dislocations, vacancies, interstitials, etc.).

Origins of martian hematite: Comparison of diffractograms of the smallest hematite crystallites (e.g. for Bardou: 5-6 nm) from Gale crater to typical hematite formed on Earth due to weathering (no contribution of diagenesis) shows significant differences between broadening of (104) and (110) peaks (Fig. 1a). For terrestrial hematite the peak (104) is 2-3 times broader than the peak (110), while for hematite samples from Gale crater both peaks are broad and of near equal FWHM. Such variations are indicative of differences in shape between martian and terrestrial hematite.

Larger sizes in a-b plane of terrestrial hematite indicate platy shape which can be related to ferrihydrite precursor and/or slow direct precipitation from solution.

Calculated crystallite sizes indicate that for the martian hematite these sizes are substantially smaller comparing to the terrestrial ones, especially in the a-b crystallographic directions and are typically equant (Fig. 1b). Such size and shape can be related to direct precipitation of martian hematite by dehydration of Fe(OH)_3 [10] or Fe(III) hydrolysis [11], and shorter crystallization time compared to terrestrial hematite.

Crystallite growth of martian hematite: Evolution of mean crystallite sizes for (104) and (110) peaks (Fig. 1b) shows that hematite at Gale Crater grows equally in all a-b-c crystallographic directions, retaining its equant shape. Among the studied samples the difference in

sizes is substantial, with the mean size more than 10 times larger for the largest crystallites (~40 nm) comparing to the smallest ones (~2-3 nm; Fig. 1b).

Calculated lognormal distributions of crystallite sizes showed that samples with larger hematite crystallites (ex. Stoer) do not show high contributions of small <10 nm crystallites. Thus, during growth, small crystallites are not retained, suggesting the mechanism of growth is rather Ostwald ripening or crystal agglomeration in closed systems. Open-system crystal growth mechanisms, such as surface-controlled growth, are less likely, as there should be substantial amounts of small crystallites, which are not clearly observed.

Implications: An increase in crystallite size going down section suggests burial diagenesis affected hematite crystallization in Gale crater. Crystallite growth in closed systems is consistent with a lack of substantial changes in geochemistry along much of the traverse [e.g., 12].

References: [1] Blake D. F. et al. (2012) *SSR*, 170, 341–399. [2] Rampe E. B. et al. (2020) *Geochemistry*, 80, 125605. [3] Blake D. F. et al. (this meeting). [4] Tu V. M. et al. (2021) *Minerals*, 11(8), 847. [5] Rampe E. B. et al. (2020) *JGR*, 125, e2019JE006306. [6] Fraeman A. A. et al. (2013) *Geology*, 41, 1103–1106. [7] Dera P. et al. (2013) *High Press. Res.*, 33, 466-484. [8] Scardi P. et al. (2018) *J. Appl. Cryst.*, 51, 831-843. [9] Balzar D. (1999) In: Defect and Microstructure Analysis by Diffraction, 94-126. [10] Pinto S. P et al. (2019) *J. Braz. Chem. Soc.*, 30, 310-317. [11]